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PRELIMINARY ANALYSIS OF AN EXTENSIVE ONE YEAR SURVEY OF TRACE ELEMENTS AND COMPOUNDS IN THE SUSPENDED PARTICULATE MATTER IN CLEVELAND, OHIO

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TECHNICAL PAPER proposed for presentation at Earth Environmental Resources Conference Philadelphia, Pennsylvania, August 10-12, 1974 PRELIMINARY ANALYSIS OF AN EXTENSIVE ONE YEAR SURVEY OF TRACE ELEMENTS AND COMPOUNDS IN THE SUSPENDED PARTICULATE MATTER IN CLEVELAND, OHIO

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Beginning in 1971 a cooperative program has been carried on by the City of Cleveland Division of Air Pollution Control and NASA Lewis Research Center to study the trace element and compound concentrations in the ambient suspended particulate matter in Cleveland, Ohio as a function of source, monitoring location and meteorological conditions. The major objectives were to determine the ambient concentration levels at representative urban sites and to develop a technique using trace element and compound data in conjunction with meteorological conditions to identify specific pollution sources which could be developed into a practical system that could be readily utilized by an enforcement agency.

Figure 1 shows a network of 16 stations whose locations were selected to provide representation for all segments of the city (population, industry, etc.). It was operated approximately every third day from August, 1971 through June, 1973. High volume samplers equipped with flow rate recorders and motor speed control regulators were installed at each of these sites. The selection of Whatman No. 41 as the filter medium permitted the use of instrumental neutron activation analysis (INAA) as the primary analytical method. a technique capable of readily detecting up to 60 elements nondestructively and with a minimum of sample preparation, thus providing analysis at a low cost per element. Five additional elements unavailable by INAA were determined by emission spectroscopy. Filters were handled in the laboratory with rubber or plastic gloves and in the field in a filter holder cassette previously loaded in the laboratory. Filters were equilibrated at less than 50% relative humidity for at least 24 hours prior to weighing; three blanks were weighed each time to correct for changes in filter weight due to relative humidity changes.

The annual means of 18 elements for Cleveland are shown in the first column in Figure 2. Values found at Heidelberg, Paris, East Chicago, Illinois and Niles, Michigan are also listed. Only tin is higher in value than for the other sites; no element is lower. Thus the values in Cleveland on the average generally are in between the highest and lowest shown.

Figure 1 also shows 7 monitoring sites in the suburbs west of Cleveland, the direction from which the wind predominantly blows. Comparison of the values for 23 elements and the value for TSP from these suburban locations covering a period of 5 to 8 days in 1972 with those from the city is made in Figure 3. Also shown is the ratio of the city values to the suburban values (U/S). The ratio of 2.7 for TSP can be used as a measure as it represents the general increase in particulate matter in the city over the suburbs. Thus, ratios higher than 2.7 indicate specific elemental sources. In this category are beryllium, chlorine, chromium, cobalt, antimony and bismuth. Iron, though high at monitoring sites near the steel mills, on the average barely exceeds the TSP ratio.

The cause for the overall high value of antimony in the city is unresolved; sources for specific locations, however, are discussed later. The values of 5-10 ng/m³ for vanadium classify the Cleveland area as a low oil burning area.

The average bromine to lead ratio in the city is ,258 while in the suburbs it is .35. Both values are in the range of .21 \pm .15 which indicates auto fuel as the source. The annual means for the sixteen monitoring sites in Cleveland varied from .21 to .32 and were well within range for gasoline, but certain sites showed higher ratios (higher bromine values) for northerly winds, indicating possible local sources other than gasoline. Only lead of all the elements determined approaches any recognized toxic levels.

Trace elements can be used for source detection and identification. For example, in Figure 4, the values for cadmium and antimony are shown at each of the monitoring sites. Two sites are notable - the southern one (13) is east of and predominantly downwind of a chemical plant that manufactures antimony oxide. The other site (6) is north and downwind generally about 30% of the time from an electric light filament plant. The different cadmium to antimony ratios at these sites substantiate the differing manufacturing operations.

Where valid wind data is available, concentration roses can be plotted for elements at monitoring sites. Figure 5 shows antimony at a predominantly suburban site and points to a strong source to the northeast believed to be a municipal incinerator about 1-1/2 miles away. Antimony is again shown in Figure 6 at a monitoring site adjacent to a power plant and the strong spike at NNW points directly at it. The spike in the NE direction points also to a power plant, but it is somewhat more distant and has a higher stack.

Sulfate, nitrate, fluoride, and pH content of TSP were also determined. Values found covering $6-\hat{o}$ days were generally lower than those reported in the literature. In addition, the ambient sulfur dioxide values didn't correlate with the sulfate values.

Ten polynuclear aromatic hydrocarbons were determined. Benzapyrene annual mean values were somewhat lower than those generally reported. The average across the city was $0.87~\text{ng/m}^3$, but maxima as high as $130~\text{ng/m}^3$ were observed adjacent to a coke oven operation.

Carbon content of TSP was also determined and varied from about 6% to 18%, the average value being 9.3%. The difference in values for residential and industrial sites is surprisingly small.

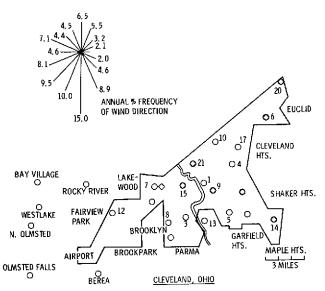


Figure 1. - Air monitoring network.

| ELEMENT | URBAN | SUBURBAN | RATIO U/S |
|---------|-------------------------|--------------------------|-----------|
| Be | 0, 14 NG/M ³ | 0, 023 NG/M ³ | 6.1 |
| Na | 850 | 360 | 2.4 |
| Mg | 1180 | 500 | 2.4 |
| Al | 2910 | 1700 | 1.7 |
| Si | 9020 | 4970 | 1.8 |
| či | 1540 | 237 | 6.5 |
| Ca | 3630 | 1810 | 2.0 |
| V | 10. 5 | 5.96 | 1, 8 |
| Cr | 18.9 | 3. 41 | 5.6 |
| Mn | 148 | 66.3 | 2, 2 |
| Fe | 4450 | 1590 | 2, 8 |
| Co | 2.58 | 0.75 | 3.4 |
| Cu | 130 | 72,0 | 1.8 |
| Zn | 413 | 264 | 1.6 |
| As | 17,5 | 12.1 | 1.4 |
| Se | 4, 7 | 3. 30 | 1.3 |
| Br | 196 | 158 | 1.2 |
| Cd | 3,9 | 1.55 | 2.5 |
| Sn | 99. 3 | 54.9 | 1.8 |
| Sb | 43, 4 | 6.3 | 6.9 |
| Hg | 0.58 | 0, 22 | 2.6 |
| РĎ | 759 | 451 | 1.7 |
| Bi | 1.26 | 0.37 | 3.4 |
| TSP | 118 000 | 44 000 | 2.7 |

Figure 3. - Comparison of average urban and suburban concentrations.

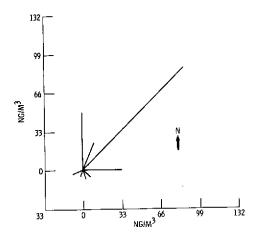


Figure 5. - Concentration rose for antimony at George Washington elementary school.

| ELEMENT | CLEVELAND 1971 | HEIDELBERG 1971 | PARIS BELOT (1971) | EAST CHICAGO, U. S. A. DAMS (1970) | NILES, MICHIGAN U. S. A. DAMS (1970) |
|---------|-------------------|--------------------|-----------------------|--|--|
| CI | 1540 | 153 | 7063 | (a) | (a) |
| La | 2.5 | 0.62 | 3, 42 | 5, 9 | 1.3 |
| Na | 850 | 224 | 1823 | 455 | 170 |
| Co | 2.6 | 2.2 | 6.67 | 2,6 | 0.95 |
| in. | 0.1 | 0, 24 | (a) | 0, 1 | 0, 04 |
| Fe | 4450 | 104L | 3500 | 13 800 | 1900 |
| Sc | 0.7 | 0, 50 | 0,70 | 3, 1 | 1, 2 |
| Mn | 148 | 23.6 | 82, 5 | 255 | 62 |
| Cs | 0.5 | 0, 57 | (a) | (a) | (a) |
| Br | 196 | 30, 5 | 433 | 67 | 32 |
| Aq | 1.1 | 4. 2 | (a) | 2.4 | l |
| Sb | 43 | 5. 1 | 50.8 | 25 | 5.8 |
| Cd | 3.9 | 26.8 | 19.5 | (a) | (a) |
| Čr | 19 | 4, 6 | 15.1 | 113 | 9.5 |
| Hg | 2. 6 | 0.17 | 11.2 | 4.8 | 1.9 |
| Sn | 99 | 71.6 | (a) | (a) | (a) |
| Ce | 4,9 | 1.0 | 14.0 | 13 | 0, 82 |
| Sm | 0.36 | 0, 24 | 0, 42 | 0, 41 | 0, 24 |

aCONCENTRATION BELOW DETECTION LIMIT.

Figure 2. - Comparison of trace elements in five cities in NG/M^3 .

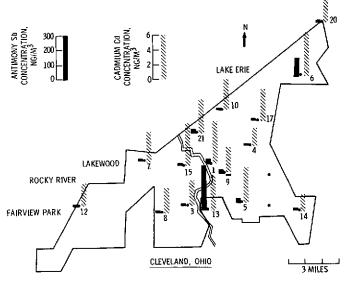


Figure 4. - Comparison of antimony and cadmium concentrations.

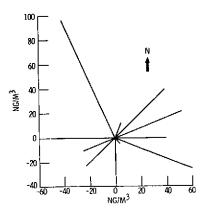


Figure 6. - Concentration rose for antimony at fire station 19.